Low Cost Air Separation Process for Gasification Applications

Gökhan Alptekin, PhD
TDA Research, Inc.
Wheat Ridge, CO
galptekin@tda.com

2017 Gasification Systems Project Review

DE-FE0026142
October 1, 2015 – March 31, 2018

March 20, 2017

TDA Research Inc. • Wheat Ridge, CO 80033 • www.tda.com
Project Goals and Objective

• The project objective is to demonstrate techno-economic viability of a new air separation technology that can be integrated into the coal gasification processes

• A high temperature chemical absorbent selective for O₂ removal is the key for the process
  • Early proof-of-concept demonstrations in an SBIR Phase II project and NETL project (DE-FE-0024060) proved high oxygen uptake and stable performance

• Project Tasks
  • Sorbent production scale-up
  • Bench-top demonstration of life (minimum 12,500 cycles)
  • Design of a fully-equipped prototype unit to fully demonstrate the concept at the bench-scale (1 kg/hr O₂ production rate)
  • Concept demonstration
  • Process design & cost analysis by Aspen Plus™ simulations
    • IGCC power generation and CTL
Project Partners

Project Duration
- Start Date = October 1, 2015
- End Date = March 31, 2018

Budget
- Project Cost = $1,600,000
- DOE Share = $1,280,000
- TDA and its partners = $320,000
Presentation Outline

- Background
- TDA’s Approach
- System Design
- Bench-Scale Results
- Modeling Results
- Prototype Unit Design
- Techno-economic Analysis
- Future Plans
• Oxygen-blown gasifiers provide smaller size and higher efficiency
  • Substantially lower NO\textsubscript{x} generation in IGCCs
  • Improved gas purity with the removal of N\textsubscript{2} in CTL processes

• ASU is one of the largest cost items in a gasification plant (consumes over 5% of plant power and constitutes ~15% of plant cost)

• Cryogenic air separation is the choice of technology at large-scale
  • 600 MW IGCC plant requires ~170 ton O\textsubscript{2}/day

• Cryo-separation is highly energy intensive due to the thermal inefficiencies inherent in the low operating temperatures
TDA’s Approach

- TDA’s process uses a unique sorbent material to carry out an oxidation-reduction (redox) process

\[ A_x B_y O_z + nO_2(g) \leftrightarrow A_x B_y O_{z+2n} \]

- Unlike conventional chemical looping combustion sorbents that also work via a similar redox cycle, the oxygen in our sorbent is released by changing process conditions

- The oxidized metal oxide phase is “meta-stable” and auto-reduces by changing T, P, oxygen partial pressure
  - The auto-reduction releases oxygen, which can be recovered as a pure product
  - No use of reducing gases (e.g., CH₄, H₂, CO, syngas) which will consume oxygen
Separation Process

- **Sorbent removes the oxygen from the high pressure air**
  - 90-95% of the oxygen is selectively removed
  - The vitiated high pressure air (that is mostly N\textsubscript{2}) is utilized in a gas turbine after boosting the pressure

- **Regeneration is carried out at low pressure close to ambient pressure using a warm sweep gas (superheated steam) ideally under isothermal conditions**
  - The combined pressure swing and concentration swing (i.e., the partial pressure difference) is used to drive O\textsubscript{2} from the sorbent

- **Temperature swing assisted Pressure swing and Vacuum swing are feasible but not economical**
System Design

Absorption Process

- GT Air
- Booster Compressor
- Heat Exchanger
- Additional Air for Added Power
- To Combustor
- Compressor
- Heat
- 

Regeneration Process

- Water
- 
- Heat Recovery Steam Generator
- LP Steam and Natural Gas
- O₂ Regeneration
- O₂
Cycle Sequence

- **Vitiated Air**: Feed/Adsorption
  - P = 15 bar

- **N₂ & inerts**: Co-BD
  - P = 15 → 3 bar

- **Steam**: Cn-BD
  - P = 2 → 1 bar

- **Purge**: O₂ rich product in steam
  - P = 1.1 bar

- **Pressurization**: Feed Air
  - P = 1.1 → 15 bar

<table>
<thead>
<tr>
<th>Bed 1</th>
<th>Adsorption</th>
<th>Co-BD</th>
<th>Cn-BD</th>
<th>Purge</th>
<th>Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed 2</td>
<td>Purge</td>
<td>Press</td>
<td>Adsorption</td>
<td>Co-BD</td>
<td>Cn-BD</td>
</tr>
<tr>
<td>Bed 3</td>
<td>Co-BD</td>
<td>Cn-BD</td>
<td>Purge</td>
<td>Press</td>
<td>Adsorption</td>
</tr>
</tbody>
</table>
Integrated with IGCC Power Plant

Process Scheme #1

Coal Handling → Gasifier → Cooler & Scrubber → Water Gas Shift → Sulfur Removal → Sulfuric Acid Plant

O₂

Steam

H₂ rich syngas

CO₂ 2200 psig

Stack Gas

Warm Gas CO₂ Separation, Purification & Compression System

Advanced ASU

Regeneration

Absorption

H₂ slipstream to supply heat to ASU

Air

Gas Turbine

Flue Gas

20 psig Steam

Stack Turbine

HRSG
Integration to Oxy-Combustion

The diagram illustrates the integration of Oxy-Combustion technology in a coal-fired power plant. The process begins with the coal entering the Coal Boiler, where it is oxidized in the presence of oxygen and carbon dioxide. The resultant CO₂ and water (H₂O) are then sent to a reduction step. Steam is produced in a steam cycle, which is used for power generation. CO₂ is captured and sent to a cooler for compression and sequestration.

The Air enters the Oxidation step, where it is preheated using the heat recovered from the Steam Generation process. This heat is used to reduce the CO₂ in the CO₂ for Compression Sequestration process, thereby completing the cycle.
Sorbent Optimization

- Oxygen release was documented over a wide range of temperatures
  - Early work (DE-FE0024060) focused on improving activity at lower temperatures
Impact of Pressure

GHSV = 500 h\(^{-1}\), T = 750, 800\(^\circ\)C, P\(_{\text{abs}}\) = 12-253 psig, P\(_{\text{des}}\) = 12 psig

- Capacity increases at higher adsorption pressure
Impact of Cycle Time

GHSV = 500 h\(^{-1}\), T = 800°C, P\(_{\text{abs}}\) = 150 psig, P\(_{\text{des}}\) = 12 psig

Shorter cycles provided the best sorbent utilization or hourly working capacity
Sorbent Working Capacity

GHSV = 500 h\(^{-1}\), T = 800°C, P\(_{\text{abs}}\) = 300 or 150 psig, P\(_{\text{des}}\) = 12 psig

<table>
<thead>
<tr>
<th>Adsorption pressure [psig]</th>
<th>Sorbent Capacity</th>
<th>Cycles completed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Per cycle [kg O(_2)/kg sorbent/cycle]</td>
<td>Per hour [kg O(_2)/kg sorbent/hr]</td>
</tr>
<tr>
<td>300</td>
<td>2.54%</td>
<td>0.157</td>
</tr>
<tr>
<td>100</td>
<td>0.52%</td>
<td>0.052</td>
</tr>
</tbody>
</table>

Higher pressures in the IGCC condition provides three times higher working capacity.

Diagram: Sorbent Capacity per Hour

- 800°C, P\(_{\text{ads}}\)=300 psig, P\(_{\text{des}}\)=12 psig, counter current purge
- Reduced cycle time

Diagram: Sorbent Capacity per Hour

- 800°C, P\(_{\text{ads}}\)=100 psig, P\(_{\text{des}}\)=12 psig, counter current purge
Multiple Cycle Tests

- Sorbent showed a stable cyclic capacity of over 2.5% wt. O₂ at 750°C

Cycle time doubled

T = 750°C
Project Structure - DE-FE0026142

October 1, 2015 – March 31, 2018

- Task 1. Project Management and Planning
- Task 2. Sorbent Production Scale-up
- Task 3. Sorbent Life Test (12,500 cycles)
- Task 4. Adsorption, CFD Modeling and Reactor Housing Design
- Task 5. Optimization of Cycle Sequence
- Task 6. Design of Prototype Unit (1 kg/hr O₂ Output)
- Task 7. Fabrication of the Prototype
- Task 8. Proof-of-Concept Demonstrations with the Prototype Unit
- Task 9. Techno-economic Analysis
Project Schedule

Task Schedule:

<table>
<thead>
<tr>
<th>Task Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1. Project Management and Planning</td>
</tr>
<tr>
<td>Task 2. Sorbent Production Scale-up</td>
</tr>
<tr>
<td>Task 3. Sorbent Life Test (12,500 cycles)</td>
</tr>
<tr>
<td>Task 4. Adsorption, CFD Modeling and Reactor Housing Design</td>
</tr>
<tr>
<td>Task 5. Optimization of Cycle Sequence</td>
</tr>
<tr>
<td>Task 6. Design of the 1 kg/hr Prototype Unit</td>
</tr>
<tr>
<td>Task 7. Fabrication of the 1 kg/hr Prototype Unit</td>
</tr>
<tr>
<td>Task 8. Testing of the Prototype Unit</td>
</tr>
<tr>
<td>Task 9. Techno-economic Analysis</td>
</tr>
<tr>
<td>Reporting</td>
</tr>
<tr>
<td>Decision Points</td>
</tr>
</tbody>
</table>

LEGEND: Plan [ ] Completed [ ] Scheduled Milestone [ ] TDA Research [ ] Revised Plan [ ] Reports [ ] Q, AR, FR [ ] Completed Milestone [ ]
Sorbent Production Scale-up

- Early work batch size 0.1 to 0.5 kg
- Current batch size 1 to 10 kg
- Target batch size (End of Task 2) 100 kg
  - The scale-up work is carried out at TDA’s pilot production facility Golden, CO using high throughput production equipment

- We will develop a Manufacturing and Quality Assurance Plans to ensure consistency in the sorbent material within each batch and minimize any batch-to-batch variations
The sorbent achieves very high equilibrium capacity above 6% wt. at a low temperature of 650°C.

In these tests we ensured complete regenerations between each data point to obtain the maximum possible capacity.

An predictive model is being built by University of Alberta.
Equilibrium isotherms were modeled using a simple Langmuir Isotherm

Isotherm model parameters were used to simulate the breakthrough curves

These simple models were able to replicate the heat effects and the average breakthrough time

These models are now being refined for use in cycle optimization
To assist with the reactor design, GTI is carrying out CFD modeling work.

- Model calibrations based on the bench-scale results are completed.
- The lab measurements and model predictions indicate modest temperature increase due to the reaction exotherm (the temperature rise between 60-110°C is predicted based on operating conditions).

The model results are used in the design of the 1 kg/hr prototype.

- It will now be used for full-scale system.
Sorbent achieves a high hourly working capacity at short cycle times
- Less than 20 min
- **Hourly working capacity**
  - 4.6% wt. O₂ at 800°C
  - 1.4% wt. O₂ at 700°C
  - 1% wt. at 600
We designed a 4-bed high temperature PSA system
Reactor Design

Vessel Sizing for 1 kg/hr O₂

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O₂ Product Rate</strong></td>
<td>1</td>
<td>kg/h</td>
</tr>
<tr>
<td><strong>O₂ Product Rate</strong></td>
<td>16.7</td>
<td>g/min</td>
</tr>
<tr>
<td><strong>Sorbent Capacity</strong></td>
<td>1.57%</td>
<td>wt. O₂</td>
</tr>
<tr>
<td><strong>Sorbent density</strong></td>
<td>0.793</td>
<td>kg/L</td>
</tr>
<tr>
<td><strong>Cycle time</strong></td>
<td>30</td>
<td>min</td>
</tr>
<tr>
<td><strong>Sorbent needed</strong></td>
<td>31.8</td>
<td>kg</td>
</tr>
<tr>
<td><strong>Total Sorbent Volume</strong></td>
<td>40.2</td>
<td>L</td>
</tr>
<tr>
<td><strong>Sorbent Volume (1 Bed)</strong></td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

- 6” diameter 36” height vessels to house 12L (0.4 CF) sorbent
- Incoloy HT is chosen for the material with a design temperature of 850°C and pressure of 300 psig
Prototype Unit Layout

- The design is completed
- All component identified and ordered
TDA in collaboration with University of California, Irvine is carrying out a high fidelity process design and economic analysis.

TDA’s ASU unit provides significant improvement in overall plant performance: an increase in the net plant efficiency from 32% to 33.74% for an IGCC power plant equipped with a cold gas cleanup system (compared to a cryogenic ASU).

The efficiency also improvement for the IGCC power plant with warm gas cleanup system:
- 35.09% vs 34.46%

The 1st year Cost of Electricity (COE) and the Cost of CO₂ Capture are also lower for the TDA ASU than for the cryogenic ASU.

Cost of CO₂ capture goes from $47 to $43 per tonne for cold gas capture and from $41 to $39 per tonne for warm gas capture.

The efficiency benefits are also demonstrated for a supercritical pulverized coal oxy-combustion power plant:
- Net plant efficiency increased from 29.3% (for a cryogenic ASU) to 30.7% (TDA ASU)
## Process Techno-economic Analysis

<table>
<thead>
<tr>
<th>Case</th>
<th>Type Plant</th>
<th>ASU Technology</th>
<th>CO₂ Capture, %</th>
<th>Gross Power Generated, kWe</th>
<th>Gas Turbine Power</th>
<th>Steam Turbine Power</th>
<th>Syngas/Air Expander</th>
<th>Auxiliary Load, kWe</th>
<th>Net Power, kWe</th>
<th>Net Plant Efficiency, % HHV</th>
<th>Coal Feed Rate, kg/h</th>
<th>Raw Water Usage, GPM/MWe</th>
<th>Total Plant Cost, $/kWe</th>
<th>COE without CO₂ TS&amp;M, $/MWh</th>
<th>COE with CO₂ TS&amp;M, $MWH</th>
<th>Cost of CO₂ Capture, $/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1A</td>
<td>IGCC – Cold Gas Cleanup - Selexol^TM GE Gasifier</td>
<td>Cryogenic</td>
<td>90</td>
<td>727,370</td>
<td>464,000</td>
<td>257,403</td>
<td>5,968</td>
<td>192,927</td>
<td>534,443</td>
<td>32.00</td>
<td>221,584</td>
<td>10.92</td>
<td>3,359</td>
<td>133</td>
<td>142</td>
<td>47</td>
</tr>
<tr>
<td>Case 1B</td>
<td>IGCC – Warm Gas Cleanup – TDA Sorbent - GE gasifier</td>
<td>TDA Sorbent</td>
<td>90</td>
<td>736,376</td>
<td>464,000</td>
<td>263,488</td>
<td>8,888</td>
<td>170,247</td>
<td>566,129</td>
<td>33.74</td>
<td>222,570</td>
<td>9.35</td>
<td>3,232</td>
<td>128</td>
<td>136</td>
<td>43</td>
</tr>
<tr>
<td>Case 2</td>
<td>SCPC – Oxy-combustion</td>
<td>TDA Sorbent</td>
<td>99.5</td>
<td>674,331</td>
<td>417,554</td>
<td>246,746</td>
<td>10,031</td>
<td>120,661</td>
<td>553,671</td>
<td>34.46</td>
<td>213,013</td>
<td>10.55</td>
<td>3,212</td>
<td>126</td>
<td>134</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>39</td>
</tr>
</tbody>
</table>

- **ASU Technology**: Cryogenic, TDA Sorbent
- **CO₂ Capture**: 90%, 90%, 90%, 90%, 99.5%
- **Gross Power Generated**: 727,370 kWe, 736,376 kWe, 674,331 kWe, 735,358 kWe, 817,314 kWe
- **Gas Turbine Power**: 464,000 kW, 464,000 kW, 417,554 kW, 464,000 kW, - kW
- **Steam Turbine Power**: 257,403 kW, 263,488 kW, 246,746 kW, 260,809 kW, 731,607 kW
- **Syngas/Air Expander**: 5,968 kW, 8,888 kW, 10,031 kW, 10,549 kW, 85,707 kW
- **Auxiliary Load**: 192,927 kW, 170,247 kW, 120,661 kW, 142,079 kW, 267,314 kW
- **Net Power**: 534,443 kW, 566,129 kW, 553,671 kW, 593,279 kW, 550,000 kW
- **Net Plant Efficiency**: 32.00%, 33.74%, 34.46%, 35.09%, 30.7%
- **Coal Feed Rate**: 221,584 kg/h, 222,570 kg/h, 213,013 kg/h, 224,161 kg/h, 224,159 kg/h
- **Raw Water Usage**: 10.92 GPM/MWe, 9.35 GPM/MWe, 10.55 GPM/MWe, 10.51 GPM/MWe, 13.92 GPM/MWe
- **Total Plant Cost**: 3,359 $/kWe, 3,232 $/kWe, 3,212 $/kWe, 3,175 $/kWe, 3,849 $/kWe
- **COE without CO₂ TS&M**: 133 $/MWh, 128 $/MWh, 126 $/MWh, 124 $/MWh, 140 $/MWh
- **COE with CO₂ TS&M**: 142 $MWH, 136 $MWH, 134 $MWH, 132 $MWH, 151 $MWH
- **Cost of CO₂ Capture**: 47 $/tonne, 43 $/tonne, 41 $/tonne, 39 $/tonne, - $/tonne
Future Work

- TDA will complete the fabrication and testing of the 1 kg/hr prototype unit demonstrating the high temperature air separation process.
- The results will allow us to further validate the CFD and absorption cycle models.
- The performance results will also be used to revise the process models being developed by UCI.
- Revise our estimates for the cost of CO$_2$ capture for GE and E-Gas gasifier based IGCC power plants and oxy-combustion coal fired power plant.